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(54) Production of L-ascorbic Acid

(57) A process for the production of L-ascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation under pressure at a temperature of at least 80°C. and with the addition of a lower alcohol after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow, i.e. there is no back-mixing.

The process may be carried out in an apparatus comprising a tube reactor having a heat exchanger and a holding tube, the inlet side of the tube reactor being connected to a metering pump and the outlet side thereof to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising L-ascorbic acid.

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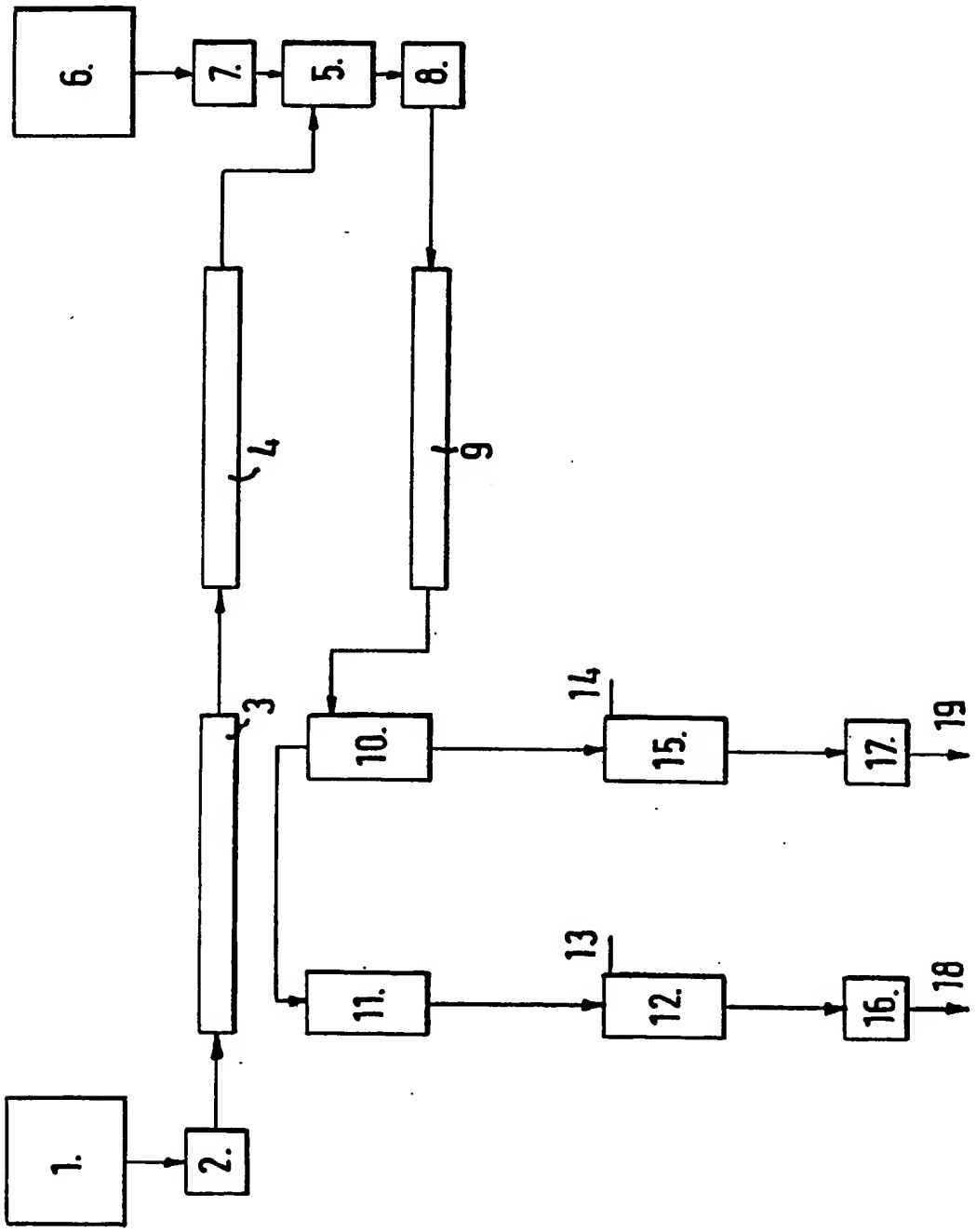

SPECIFICATION

Process and Device for Producing L-ascorbic Acid

The present invention is concerned with a process and a device for producing L-ascorbic acid from L-keto-gulonic acid or derivatives thereof.

It is known that warming L-ketogulonic acid or derivatives thereof with acids, for example hydrochloric acid, results in an enolisation/lactonisation to L-ascorbic acid taking place.

Under acidic conditions, the synthesis can only be carried out optimally if the reaction time is kept within a narrow range and the acidic catalyst is substantially removed after the reaction has taken place. The isolation of the acidic catalyst from the reaction mixture is the main problem of the acid enolisation because an almost quantitative crystallisation of the ascorbic acid cannot take place in the presence of mineral acids.

Processes have been described in which hydrochloric acid is generally used as the volatile mineral acid. This is separated from the enolisation mixture by adding, before or after the enolisation reaction, short-chain halogenated hydrocarbons, lower alcohols or possibly aromatic hydrocarbons in order to remove hydrochloric acid and water by entrainment distillation. The ascorbic acid is then crystallised and purified in known manner.

The previously described synthesis variations give yields of up to 90% of ascorbic acid, the purity of which is from 94 to 99%.

Disadvantages of the previously described methods of preparation include the very long reaction times and consequently large apparatus volumes, working up of the materials required for the removal of hydrochloric acid by entrainment distillation, the continuous lowering of the catalyst concentration by fractional distillation and, in the case of using an alcohol, the formation of large quantities of alkyl halide, the saponification of which requires additional expenditure.

It is an object of the present invention to carry out the acid-catalysed enolisation/lactonisation of L-ketogulonic acid or of its drivatives in such a manner that, with low energy and adjuvant costs and with essentially shorter reaction times, high ascorbic acid yields are obtained with a high throughput per unit volume, the main steps of the new process being continuous and the isolation of the acidic catalyst taking place under mild conditions in a very short time and with only one adjuvant.

A further object of the present invention is to provide a large-scale continuous process for producing L-ascorbic acid in high yields in such a manner that the isolation of the crude ascorbic acid from a mineral acid solution takes place by evaporating the hydrohalic acid catalyst with an alcohol as adjuvant.

The contact time between the alcohol used and the mineral acid-containing enolisation mixture is to be as short as possible in order substantially to avoid the formation of alkyl halide. The remaining mineral acid concentration must be kept as low as possible since otherwise a quantitative crystallisation of the ascorbic acid does not take place.

Thus, according to the present invention, there is provided a process for the production of L-ascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation, for example with hydrochloric acid, under pressure at a temperature of at least 80°C. and preferably of 80 to 110°C. and with the addition of a lower alcohol, for example *n*-butanol, after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow. Thus, for example, the residence time of the reaction mixture in the tube reactor can be from 5 to 15 minutes.

According to a preferred embodiment of the process according to the present invention, the enolisation-lactonisation reaction is stopped by the addition of *n*-butanol and a mixture of *n*-butanol and hydrochloric acid is immediately evaporated off by the use of a high supply of heat per unit surface area, crude ascorbic acid being isolated as a sump product in a subsequent packed column.

The present invention also provides a device for carrying out the process, comprising a tube reactor system having a heat exchanger and a holding tube, the inlet side of the tube reactor system being connected to a metering pump and the outlet side thereof being connected to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising L-ascorbic acid.

For a better understanding of the present invention, one embodiment of the device according to the present invention will now be described in more detail, with reference to the accompanying drawings.

The invention essentially requires a combination of a heat exchanger (3), a holding tube (4), a long-tube evaporator (9) and a separation column (10).

The acid starting mixture to be enolised is pumped by means of a metering pump (7) through (3) and (4) at a temperature of 80 to 110°C.

The flow rate of the reaction mixture through (3) and (4) is so adjusted that the residence time behaviour of the reacting molecules approximates to that of a plug flow, i.e. counteracts back-mixing.

The residence time in the above-mentioned temperature range is preferably 5 to 15 minutes and the pressure is preferably maintained at 3—8 ats. In a mixing chamber (5) arranged downstream from the holding tube (4) *n*-butanol is added continuously by a metering pump (7) from a reservoir (6), which results in an immediate reduction of the reaction mixture temperature so that no further reaction takes place. The butanolic enolate then passes through a pressure valve (8) and, under reduced pressure, is immediately evaporated in a long-tube evaporator (9) so that equilibration between vapour and liquid is avoided as completely as possible.

In this way, more than 90% of the hydrochloric acid is removed at an evaporation rate of less than 1 second. This result is surprising because, in the case of normal distillation, butanol is unsuitable for entraining hydrochloric acid.

The actual separation of the volatile components, i.e. alcohol and hydrochloric acid, takes place in a packed column (10). The top gases and vapours from the column (10) are passed to a condenser (11) for the alcohol and the condensate obtained is passed to an alcohol reservoir (12) having a connection (13) to a centrifuge. Alcohol is removed from reservoir (12) by a pump (16) and passed through pipe (18) to be worked up for further use.

The sump from the packed column (10), which contains the L-ascorbic acid is passed to a crystalliser cascade (15) provided with a vacuum connection (14). The crystallised L-ascorbic acid is then removed, *via* pump (17), through outlet (19).

The economic effectiveness of the present invention manifests itself in that, for the first time, there is provided a continuous process and device which permit substantially reduced reaction times for the enolisation-lactonisation of L-ketogulonic acid.

The entraining agent for the removal of the acid catalyst can be recovered simply and almost quantitatively. The removal of the acidic catalyst has been technically resolved in such a manner that this operation takes less than one second. The resultant low thermal stress on the reaction mixture means that almost no by-products, such as hydrocarbon halogen derivatives and ethers of the alcohol, are formed.

The high throughput with a small volume capacity of the enolisation plant enables production to be carried out in a small space with low manpower needs.

The following Examples are given for the purpose of illustrating the present invention:—

Example 1

A suspension of diacetone-1-ketogulonic acid (DAKGA) and concentrated hydrochloric acid (10.78 kg/h of DAKGA and 5.39 l/h of 36% hydrochloric acid) is pumped by a metering pump (2) from a stirrer vessel (1) through a pipeline reactor (3, 4) heated to 100°C. The feed rate is 15.1 l/h and the residence time is 10 minutes. A pressure of 6 ats is obtained, which is kept constant by means of a pressure maintenance valve (8). Before the enolate formed enters the long-tube evaporator (9), 22 l/h of *n*-butanol are added by means of a metering pump (7) from a storage tank (6) *via* mixing chamber (5). The pressure in the evaporator/column/condenser section is 80—100 mm. Hg and the temperature is 60 to 65°C. The separation of the volatile components (hydrochloric acid and butanol) takes place in a packed column (10). The crude ascorbic acid is obtained as a sump in (10). Subsequent processing and purification takes place in known manner. Yield: 6.2 kg/h of crude ascorbic acid (92% of theory); content 96.5%.

Example 2

A suspension of l-ketogulonic acid (KGA) and concentrated hydrochloric acid (10.70 kg/h of KGA and 5.35 l/h of 36% hydrochloric acid) is pumped by a metering pump (2) from a stirrer vessel (1) through a pipeline reactor (3, 4) heated to 100°C. The feed rate is 15.0 l/h and the residence time is 10 minutes. A pressure of 5.4 ats is obtained which is kept constant by means of the pressure valve (8). Before the enolate enters the long-tube evaporator (9), 22 l/h of *n*-butanol are added thereto, by means of a metering pump (7), from the storage tank (6) *via* the mixing chamber (5). The pressure in the evaporator/column/condenser section is 80 to 100 mm. Hg and the temperature is 60 to 65°C. The separation of the volatile components (hydrochloric acid and butanol) takes place in the packed column (10). The crude ascorbic acid is obtained as a liquid product. Subsequent processing and purification are carried out in known manner. Yield: 7.490 kg/h of crude ascorbic acid (87% of theory); purity: 96.6%.

Claims

1. Process for the production of L-ascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation under pressure at a temperature of at least 80°C. and with the addition of a lower alcohol after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow.

2. Process according to claim 1, wherein the residence time of the reaction mixture in the tube reactor is from 5 to 15 minutes.

3. Process according to claim 1 or 2, wherein hydrochloric acid is used as the acid catalyst.

4. Process according to any of the preceding claims, wherein the lower alcohol used is *n*-butanol.

5. Process according to claim 4, wherein the enolisation-lactonisation reaction is stopped by the addition of *n*-butanol and a mixture of *n*-butanol and hydrochloric acid is immediately

evaporated off by the use of a high supply of heat per unit surface area, crude ascorbic acid being isolated as a sump product in a subsequent packed column.

6. Process according to claim 1 for the production of L-ascorbic acid, substantially as hereinbefore described and exemplified.

7. L-ascorbic acid, whenever produced by the process according to any of claims 1 to 6.

8. Device for carrying out the process according to claim 1, comprising a tube reactor system having a heat exchanger and a holding tube, the inlet side of the tube reactor system being connected to a metering pump and the outlet side thereof to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising L-ascorbic acid.

9. Device according to claim 8 for carrying out the process according to claim 1, substantially as hereinbefore described and exemplified, with reference to the accompanying drawings.

10. L-Ascorbic acid, whenever produced with the device according to claim 8 or 9.

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Production of L-ascorbic Acid

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Abstract

A process for the production of L- ascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation under pressure at a temperature of at least 80 DEG C. and with the addition of a lower alcohol after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow, i.e. there is no back-mixing. The process may be carried out in an apparatus comprising a tube reactor having a heat exchanger and a holding tube, the inlet side of the tube reactor being connected to a metering pump and the outlet side thereof to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising L-ascorbic acid.

Description

SPECIFICATION
Process and Device for Producing L-ascorbic
Acid
The present invention is concerned with a process and a device for producing L-ascorbic acid from L-keto-gulonic acid or derivatives thereof.

It is known that warming L-ketogulonic acid or derivatives thereof with acids, for example hydrochloric acid, results in an enolisation/lactonisation to L-ascorbic acid taking place.

Under acidic conditions, the synthesis can only be carried out optimally if the reaction time is kept within a narrow range and the acidic catalyst is substantially removed after the reaction has taken place. The isolation of the acidic catalyst from the reaction mixture is the main problem of the acid enolisation because an almost quantitative crystallisation of the ascorbic acid cannot take place in the presence of mineral acids.

Processes have been described in which hydrochloric acid is generally used as the volatile mineral acid. This is separated from the enolisation mixture by adding, before or after the enolisation reaction, short-chain halogenated hydrocarbons, lower alcohols or possibly aromatic hydrocarbons in order to remove hydrochloric acid and water by entrainment distillation. The ascorbic acid is then crystallised and purified in known manner.

The previously described synthesis variations give yields of up to 90% of ascorbic acid, the purity of which is from 94 to 99%
Disadvantages of the previously described methods of preparation include the very long reaction times and consequently large apparatus volumes, working up of the materials required for the removal of hydrochloric acid by entrainment distillation, the continuous lowering of the catalyst concentration by fractional distillation and, in the case of using an alcohol, the formation of large quantities of alkyl halide, the saponification of which requires additional expenditure.

It is an object of the present invention to carry out the acid-catalysed enolisation/lactonisation of L-ketogulonic acid or of its drivatives in such a manner that, with low energy and adjuvant costs and with essentially shorter reaction times, high ascorbic acid yields are obtained w.ith a high throughput per unit volume, the main steps of the new process being continuous and the isolation of the acidic catalyst taking place under mild conditions in a very short time and with only one adjuvant.

A further object of the present invention is to provide a large-scale continuous process for producing L-ascorbic acid in high yields in such a manner that the isolation of the crude ascorbic acid from a mineral acid solution takes place by evaporating the hydrohalic acid catalyst with an alcohol as adjuvant.

The contact time between the alcohol used and the mineral acid-containing enolisation mixture is to be as short as possible in order substantially to avoid the formation of alkyl halide. The remaining mineral acid concentration must be kept as low as possible since otherwise a quantitative crystallisation of the ascorbic acid does not take place.

Thus, according to the present invention, there is provided a process for the production of Lascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation, for example with hydrochloric acid, under pressure at a temperature of at least 800C. and preferably of 80 to 11 0 C. and with the addition of a lower alcohol, for example nbutanol, after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow. Thus, for example, the residence time of the reaction mixture in the tube reactor can be from 5 to 1 5 minutes.

According to a preferred embodiment of the process according to the present invention, the enolisation-lactonisation reaction is stopped by the addition of n-butanol and a mixture of nbutanol and hydrochloric acid is immediately evaporated off by the use of a high supply of heat per unit surface area, crude ascorbic acid being isolated as a sump product in a subsequent packed column.

The present invention also provides a device for carrying out the process, comprising a tube reactor system having a heat exchanger and a holding tube, the inlet side of the tube reactor system being connected to a metering pump and the outlet side thereof being connected to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising
L-ascorbic acid.

For a better understanding of the present invention, one embodiment of the device according to the present invention will now be described in more detail, with reference to the accompanying drawings.

The invention essentially requires a combination of a heat exchanger (3), a holding tube (4), a long-tube evaporator (9) and a separation column (10).

The acid starting mixture to be enolised is pumped by means of a metering pump (7) through (3) and (4) at a temperature of 80 to 1 100C.

The flow rate of the reaction mixture through (3) and (4) is so adjusted that the residence time behaviour of the reacting molecules approximates to that of a plug flow, i.e. counteracts backmixing.

The residence time in the above-mentioned temperature range is preferably 5 to 1 5 minutes and the pressure is preferably maintained at 38 ats. In a mixing chamber (5) arranged downstream from the holding tube (4) n-butanol is added continuously by a metering pump (7) from a reservoir (6), which results in an immediate reduction of the reaction mixture temperature so that no further reaction takes place. The butanolic enolate then passes through a pressure valve (8) and, under reduced pressure, is immediately evaporated in a long-tube evaporator (9) so that equilibration between vapour and liquid is avoided as completely as possible.

In this way, more than 90% of the hydrochloric acid is removed at an evaporation rate of less than 1 second. This result is surprising because, in the case of normal distillation, butanol is unsuitable for entraining hydrochloric acid.

The actual separation of the volatile components, i.e. alcohol and hydrochloric acid, takes place in a packed column (10). The top gases and vapours from the column (10) are passed to a condenser (11) for the alcohol and the condensate obtained is passed to an alcohol reservoir (12) having a connection (13)to a centrifuge. Alcohol is removed from reservoir (12) by a pump (16) and passed through pipe (18) to be worked up for further use.

The sump from the packed column (10), which contains the L-ascorbic acid is passed to a crystalliser cascade (15) provided with a vacuum connection (14). The crystallised L-ascorbic acid is then removed, via pump (17), through outlet (19).

The economic effectiveness of the present invention manifests itself in that, for the first time, there is provided a continuous process and device which permit substantially reduced reaction times for the enolisation-lactonisation of L-ketogulonic acid.

The entraining agent for the removal of the acid catalyst can be recovered simply and almost quantitatively. The removal of the acidic catalyst has been technically resolved in such a manner that this operation takes less than one second.

The resultant low thermal stress on the reaction mixture means that almost no by-products, such as hydrocarbon halogen derivatives and ethers of the alcohol, are formed.

The high throughput with a small volume capacity of the enolisation plant enables production to be carried out in a small space with low manpower needs.

The following Examples are given for the purpose of illustrating the present invention t
Example 1
A suspension of diacetone-1-ketogulonic acid (DAKGA) and concentrated hydrochloric acid (10.78 kg/h of DAKGA and 5.39 l/h of 36% hydrochloric acid) is pumped by a metering pump (2) from a stirrer vessel (1)

through a pipeline reactor (3, 4) heated to 1 000C. The feed rate is 15.1 l/h and the residence time is 10 minutes. A pressure of 6 ats is obtained, which is kept constant by means of a pressure maintenance valve (8). Before the enolate formed enters the long-tube evaporator (9), 22 l/h of n-butanol are added by means of a metering pump (7) from a storage tank (6) via mixing chamber (5). The pressure in the evaporator/column/condenser section is 80-1 00 mm. Hg and the temperature is 60 to 650C. The separation of the volatile components (hydrochloric acid and butanol) takes place in a packed column (10). The crude ascorbic acid is obtained as a sump in (10). Subsequent processing and purification takes place in known manner. Yield: 6.2 kg/h of crude ascorbic acid (92% of theory); content 96.5%.

Example 2
A suspension of l-ketogulonic acid (KGA) and concentrated hydrochloric acid (10.70 kg/h of KGA and 5.35 l/h of 36% hydrochloric acid) is pumped by a metering pump (2) from a stirrer vessel (1) through a pipeline reactor (3, 4) heated to i 000C. The feed rate is 15.0 l/h and the residence time is 10 minutes. A pressure of 5.4 ats is obtained which is kept constant by means of the pressure valve (8). Before the enolate enters the long-tube evaporator (9), 22 l/h of n butanol are added thereto, by means of a metering pump (7), from the storage tank (6) via the mixing chamber (5). The pressure in the evaporator/column/condenser section is 80 to 100 mm. Hg and the temperature is 60 to 650C.

The separation of the volatile components (hydrochloric acid and butanol) takes place in the packed column (10). The crude ascorbic acid is obtained as a liquid product. Subsequent processing and purification are carried out in known manner. Yield: 7.490 kg/h of crude ascorbic acid (87% of theory); purity: 96.6%.

Claims

Claims

1. Process for the production of L-ascorbic acid from L-ketogulonic acid or a derivative thereof by acid-catalysed enolisation and lactonisation under pressure at a temperature of at least 800 C. and with the addition of a lower alcohol after enolisation, wherein the enolisation and lactonisation are carried out continuously in a tube reactor, the flow rate of which is so adjusted that the residence time characteristic of the reacting molecules approximates to that of a plug flow.

2. Process according to claim 1, wherein the residence time of the reaction mixture in the tube reactor is from 5 to 1 5 minutes.

3. Process according to claim 1 or 2, wherein hydrochloric acid is used as the acid catalyst.

4. Process according to any of the preceding claims, wherein the lower alcohol used is n butanol.

5. Process according to claim 4, wherein the enolisation-lactonisation reaction is stopped by the addition of n-butanol and a mixture of n butanol and hydrochloric acid is immediately evaporated off by the use of a high supply of heat per unit surface area, crude ascorbic acid being isolated as a sump product in a subsequent packed column.

6. Process according to claim 1 for the production of L-ascorbic acid, substantially as hereinbefore described and exemplified.

7. L-ascorbic acid, whenever produced by the process according to any of claims 1 to 6.

8. Device for carrying out the process according to claim 1, comprising a tube reactor system having a heat exchanger and a holding tube, the inlet side of the tube reactor system being connected to a metering pump and the outlet side thereof to a mixing chamber, the mixing chamber in turn being connected, on the one hand, to a second metering pump for feeding in an alcohol from a reservoir therefor and, on the other hand, to a pressure valve to which is connected a long-tube evaporator leading to a separating column, said separating column being connected to means for recovering the alcohol and means for crystallising L-ascorbic acid.

9. Device according to claim 8 for carrying out the process according to claim 1, substantially as hereinbefore described and exemplified, with reference to the accompanying drawings.

10. L-Ascorbic acid, whenever produced with the device according to claim 8 or 9.